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Circularly Polarized Luminescence from Enantiopure C₂-Symmetrical Tetrakis(2-pyridylmethyl)-1,2-diaminocyclohexane Lanthanide Complexes

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ABSTRACT: We report the synthesis and characterization of C_2 -symmetrical lanthanide complexes supported by enantiopure hexadentate ligands derived from 1,2-diaminocyclohexane. Coordination of (R,R)- or (S,S)-N,N,N',N'-tetrakis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane (tpdac) to samarium, europium, terbium, and dysprosium generates the corresponding C_2 -symmetrical (tpdac)Ln(OTf)₃ complexes in high yields. The tpdac ligands are competent sensitizers for lanthanide luminescence, yielding modest emissions (Φ of $\leq 28\%$). Additionally, the complexes exhibit strong circularly polarized luminescence ($|g_{lum}|$ values of up to 0.13, 0.09, 0.22, and 0.15 for Sm, Eu, Tb, and Dy, respectively) in solution. We also observed that some transitions typically associated with small dissymmetry



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factors exhibit unusually high |g_{lum}| values and, therefore, should not be overlooked in future studies.

INTRODUCTION

Circularly polarized luminescence (CPL) is the emission of light where one circular polarization (left or right) is more intense than the other (right or left, respectively). Growing interest in the field of CPL has been justified by promising applications of CPL emitters for three-dimensional displays, spintronic devices,² information storage,³ and optical sensors.⁴ CPL is quantified by luminescence dissymmetry factors $\{g_{lum} =$ $(I_{\rm L} - I_{\rm R}) / [^1 / _2 (I_{\rm L} + I_{\rm R})]$, where $I_{\rm L}$ and $I_{\rm R}$ are the intensities of the left- and right-polarized emission, respectively}. To date, the most efficient CPL emitters are lanthanide-based coordination complexes with g_{lum} values ranging from 0.1 to 1,⁵ although recent advances in CPL-emitting small molecules $(g_{\rm lum} \sim 10^{-2})^6$ and transition metal complexes $(g_{\rm lum}$ values of ≤ 0.2) have been made.⁷⁻¹¹ Due to the fact that their luminescence arises from f-f transitions, lanthanide complexes are ideal for CPL emission. For the same reason, however, lanthanide light absorption is weak and therefore requires the coordination of organic ligand sensitizers to enable their emission (the so-called "antenna effect").¹² In the concluding remarks of their review on lanthanide CPL, Zinna and Di Bari stated that optimum ligands for lanthanide-based CPL should (1) form a stable/inert lanthanide complex, (2) be a good sensitizer, (3) form a complex with chiral geometry that can give rise to strong CPL, and (4) form a complex with good solubility.^{5a} We have recently reported that simple N,N,N',N'tetrakis(2-pyridylmethyl)ethylenediamine (tpen in Figure 1) forms stable lanthanide complexes, exhibiting only one C_2 symmetrical species in solution.¹³ These lanthanide complexes are modestly luminescent and soluble in polar organic solvents

and lack only the ability to form a chiral geometry to potentially enable CPL. The chiral *trans*-1,2-diaminocyclohexane moiety has recently been shown to enable strong CPL with lanthanides using an N,N'-bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane-N,N'-diacetic acid ligand (bpcd in Figure 1).¹⁴ This dianionic ligand affords Tb and Eu complexes with g_{lum} values of $\leq |0.11|$ and $\leq |0.2|$, respectively. Inspired by our previous work and these contributions, we report herein the synthesis and circularly polarized luminescence of visible emitting lanthanide complexes (Sm, Eu, Tb, and Dy) supported by a chiral derivative of the neutral tpen [N,N,N',N'-tetrakis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane (tpdac in Figure 1)]. These complexes are modestly luminescent with quantum yields ranging from 0.2% to 28% and display strong CPL activity with g_{lum} values of $\leq |0.22|$.

RESULTS AND DISCUSSION

Synthesis and Characterization. The enantiopure ligands (R,R)-tpdac and (S,S)-tpdac were synthesized from enantiopure (R,R)-1,2-diaminocyclohexane and (S,S)-1,2-diaminocyclohexane, respectively, using a method similar to that used for the preparation of tpen (Scheme 1).¹³ Recrystalliza-

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Figure 1. Previously reported luminescent lanthanide complexes supported by neutral (tpen) and dianionic (bpcd) hexadentate ligands (left) and neutral hexadentate ligand (tpdac) complexes discussed in this work (right).

Scheme 1. Synthesis of (S,S)-tpdac and Coordination to Lanthanides^a



^aThe syntheses of the (R,R)-tpdac enantiomer and its corresponding complexes were performed analogously using (R,R)-1,2-diaminocyclohexane as starting material.

tion from hexanes yielded colorless blocks that were ground and dried; this purification step was essential for obtaining good luminescence from the subsequent coordination complexes. Coordination of tpdac ligands to lanthanide trifluoromethanesulfonate salts yielded complexes (tpdac)Ln-(OTf)₃ (Ln = Sm, Eu, Tb, or Dy) in good yields after recrystallization (Scheme 1). The ¹H NMR spectra of each enantiomer of the metal complexes were taken and, as expected, were identical. For the weakly paramagnetic ((*S*,*S*)tpdac)Sm(OTf)₃ complex, two independent sets of peaks attributed to the pyridines were observed (Figure S1). The europium, terbium, and dysprosium complexes were highly paramagnetically shifted but exhibited the expected number of peaks (Figures S3, S6, and S8, respectively).

Solid State Structures. Recrystallization of both enantiomers ((R,R)-tpdac)Eu(OTf)₃ and ((S,S)-tpdac)Eu(OTf)₃ vielded single crystals suitable for X-ray diffraction studies. As expected, both enantiomers crystallized as single enantiomers in the noncentrosymmetric $P2_12_12_1$ space group [Flack parameters¹⁵ of -0.017(2) and 0.028(6) for ((R,R)-tpdac)- $Eu(OTf)_3$ and ((S,S)-tpdac)Eu $(OTf)_3$, respectively]. The solid state structure of ((R,R)-tpdac)Eu(OTf)₃ showed the hexadentate coordination of the (R,R)-tpdac ligand to the lanthanide ion, as well as two bound trifluoromethanesulfonates and a third trifluoromethanesulfonate out of sphere (Figure 2, left). The eight-coordinate geometry around the lanthanide can be best described as a bisdisphenoid (or dodecahedral deltahedron),¹⁶ where a C_2 symmetry axis crosses the vertex formed by the oxygen atoms of the trifluoromethanesulfonate ligands (Figure S45). This structure contrasts with the previously reported (tpen)Eu(OTf)₃ complex, which is best described as a distorted square antiprism.¹³ This slight change in geometry is possibly due to the increased rigidity of the cyclohexane backbone. As expected, the solid state structure of ((S,S)-tpdac)Eu(OTf)₃ is



Figure 2. Solid state structures of ((R,R)-tpdac)Eu(OTf)₃ (left) and ((S,S)-tpdac)Eu(OTf)₃ (right). Hydrogen atoms, noncoordinated trifluoromethanesulfonate, and co-crystallized 1,2-dimethoxyethane have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 50% probability level.

a perfect mirror image of the one previously described for the ((R,R)-tpdac)Eu(OTf)₃ complex (Figure 2, right).

Luminescence Properties. The emissive properties of the recrystallized complexes (tpdac)Ln(OTf)₃ (Ln = Sm, Eu, Tb, or Dy) were investigated. Acetonitrile solutions of both enantiomers of the complexes were excited at 280 nm; their emission spectra were recorded, and as expected, each enantiomer gave identical data (Figure 3). The expected sharp transitions were observed for all visible emitting lanthanides.^{12a} Specific analysis of the ((*R*,*R*)-tpdac)Eu(OTf)₃ emission spectrum can provide additional information about the number of species in solution and the symmetry of the complex.¹⁷ A unique and sharp ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition (577 nm) was observed, as well as three components in the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (591 nm), indicative of a single species in solution (Figure 3, top right). The presence of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition, combined with the ¹H NMR and single-crystal X-ray



Figure 3. Emission spectra of $(tpdac)Ln(OTf)_3$ [Ln = Sm(S,S) (top left), Eu(R,R) (top right), Tb(S,S) (bottom left), and Dy(R,R) (bottom right)] complexes emitting in the visible region (~4.5 × 10⁻⁶ mol L⁻¹ in acetonitrile). Excitation at 280 nm. Slit widths (nm): 20/5, 20/1, 10/1, and 20/10 for Ex/Em for Sm, Eu, Tb, and Dy, respectively.

diffraction data, is consistent with a C_2 symmetry of the complex in solution. An unusually strong ${}^5D_0 \rightarrow {}^7F_4$ transition is observed at 699 nm. Because this region is often corrected for the low sensitivity of the detector, we also collected noncorrected data (Figure S42).

The quantum yields are 0.17%, 1.8%, 28.4%, and 0.43% for the samarium, europium, terbium, and dysprosium complexes, respectively. These quantum yields are lower than those of the comparable (tpen) $Ln(OTf)_3$ complexes,¹³ likely due to the increased number of C-H bonds present from the cyclohexane backbone and the resulting loss of sensitization energy through C-H vibrations.¹⁸ Utilizing the analogous gadolinium complex, the triplet energy of the tpdac ligand was determined to be around 24150 cm⁻¹ (Figure S18), which is consistent with the energy levels of the emissive lanthanide states (17700 cm^{-1} , ¹⁹ 17300 cm^{-1} , ¹⁷ 20500 cm^{-1} , ²⁰ and 21000 cm^{-1} , respectively)²¹ and the respective quantum yields observed. As expected for lanthanide-based emitters, long luminescence lifetimes were observed for the strong emitters (0.95 and 3.3 ms for Eu and Tb, respectively), while shorter lifetimes were obtained for the weakly luminescent complexes (25 and 20 μ s for Sm and Dy, respectively). Photophysical data are compiled in Table 1. Using the lifetimes and quantum yields, the sensitization efficiency was determined to be 12.1% for the europium complexes (see pages S23 and S24 of the Supporting Information).

Circularly Polarized Luminescence. The relatively good luminescence of all complexes made them available for

Table 1. Compiled Photophysical Data for $((R,R)-tpdac)Ln(OTf)_3$ and $((S,S)-tpdac)Ln(OTf)_3^a$

| | | lifetimes and CPL | | | | | | | | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|-------------------|-------------|-----------------|-----------------|--|--|--|--|--|
| | | | | g_{lu} | $g_{ m lum}$ | | | | | |
| Ln | Φ (%) | wavelength (nm) | τ (ms) | R,R | S,S | | | | | |
| Sm | 0.17 | 563 | 0.025 | +0.12 | -0.13 | | | | | |
| | | 597 | 0.025 | -0.06 | +0.05 | | | | | |
| | | 643 | 0.023 | -0.05 | +0.05 | | | | | |
| Eu | 1.8 | 577 | 0.90 | nd ^b | nd ^b | | | | | |
| | | 591 | 0.95 | -0.06 | +0.06 | | | | | |
| | | 615 | 0.96 | -0.06 | +0.06 | | | | | |
| | | 648 | 0.95 | +0.09 | -0.09 | | | | | |
| | | 690 | 0.95 | +0.07 | -0.07 | | | | | |
| Тb | 28.4 | 489 | 3.3 | +0.02 | -0.02 | | | | | |
| | | 542 | 3.3 | -0.17 | +0.16 | | | | | |
| | | 582 | 3.4 | -0.07 | +0.07 | | | | | |
| | | 622 | 3.4 | +0.10 | -0.10 | | | | | |
| | | 650 | 3.3 | -0.22 | +0.21 | | | | | |
| Dy | 0.43 | 479 | 0.020 | -0.05 | +0.05 | | | | | |
| | | 575 | 0.021 | -0.01 | +0.02 | | | | | |
| | | 665 | na | -0.15 | +0.14 | | | | | |
| ^{<i>a</i>} CPL was measured at $\sim 1 \times 10^{-3}$ mol L ⁻¹ . The lifetime was measured to be $\sim 4 \times 10^{-6}$ mol L ⁻¹ . ^{<i>b</i>} Not detectable. | | | | | | | | | | |

circularly polarized luminescence studies. Circularly polarized luminescence spectra of both enantiomers ((R,R)-tpdac)Sm-



Figure 4. Normalized CPL spectra of ((R,R)-tpdac)Sm(OTf)₃ (red) and ((S,S)-tpdac)Sm(OTf)₃ (blue) in acetonitrile solutions $(1.12 \times 10^{-3} \text{ mol } L^{-1})$ at room temperature. The intensity of each transition has been normalized to the largest CPL signal (see Figure S10 for the g_{lum} plot). The total luminescence is traced in the background. Excitation at 280 nm. Slit widths: 13 nm (Ex/Em).



Figure 5. Normalized CPL spectra of ((R,R)-tpdac)Eu(OTf)₃ (red) and ((S,S)-tpdac)Eu(OTf)₃ (blue) in acetonitrile solutions (9.27 × 10⁻⁴ mol L⁻¹) at room temperature. The intensity of each transition has been normalized to the largest CPL signal (see Figure S13 for the g_{lum} plot). The total luminescence is traced in the background. Excitation at 280 nm. Slit widths: 5 nm (Ex/Em).

 $(OTf)_3$ and ((S,S)-tpdac)Sm $(OTf)_3$ were obtained in acetonitrile. Perfect mirror image CPL spectra were recorded and display rich features (Figure 4). The most CPL-active band originates from the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition, displaying a bisignate pattern with maximum g_{lum} values of |0.12|. For the emission centered at 601 nm corresponding to the ${}^4G_{5/2} \rightarrow$ ${}^6H_{7/2}$, a more complex tetrasignate pattern is observed with maximum g_{lum} values around |0.05|. The last observable transition (${}^4G_{5/2} \rightarrow {}^6H_{9/2}$) is weaker in both intensity and g_{lum} (|0.01|) and follows a bisignate pattern. Those observations are consistent with the expected rotatory strengths of the transitions, where $R({}^4G_{5/2} \rightarrow {}^6H_{5/2}) \approx$ $R({}^4G_{5/2} \rightarrow {}^6H_{7/2}) > R({}^4G_{5/2} \rightarrow {}^6H_{9/2}).^{22}$ The CPL spectra of both enantiomers ((*R*,*R*)-tpdac)Eu-(OTf)₃ and ((*S*,*S*)-tpdac)Eu(OTf)₃, obtained in acetonitrile, also displayed perfect mirror images (Figure 5). As expected, no detectable CPL signals are observed from the ⁵D₀ \rightarrow ⁷F₀ transition. Modestly CPL-active signals were observed for the ⁵D₀ \rightarrow ⁷F₁ and ⁵D₀ \rightarrow ⁷F₂ at 593 and 615 nm, respectively, with a maximum *g*_{lum} value of ~l0.06l. Surprisingly, marginally stronger CPL signals (~l0.08l) were observed from the ⁵D₀ \rightarrow ⁷F₃ and ⁵D₀ \rightarrow ⁷F₄ at 650 and 701 nm, respectively. The latter transitions are not typically reported or do not exhibit stronger CPL signals than the typically studied ⁵D₀ \rightarrow ⁷F₁ and ⁵D₀ \rightarrow ⁷F₂ transitions.

The two enantiomers ((R,R)-tpdac)Tb $(OTf)_3$ and ((S,S)-tpdac)Tb $(OTf)_3$ also showed mirror image CPL spectra



Figure 6. Normalized CPL spectra of $((R_1,R_1)$ -tpdac)Tb(OTf)₃ (red) and $((S_1,S_1)$ -tpdac)Tb(OTf)₃ (blue) in acetonitrile solutions (9.22 × 10⁻⁴ mol L⁻¹) at room temperature. The intensity of each transition has been normalized to the largest CPL signal (see Figure S15 for the g_{lum} plot). The total luminescence is traced in the background. Excitation at 280 nm. Slit widths: 5 nm (Ex/Em).



Figure 7. Normalized CPL spectra of ((R,R)-tpdac)Dy(OTf)₃ (red) and ((S,S)-tpdac)Dy(OTf)₃ (blue) in acetonitrile solutions $(9.19 \times 10^{-4} \text{ mol } L^{-1})$ at room temperature. The intensity of each transition has been normalized to the largest CPL signal (see the Figure S17 for the g_{lum} plot). The total luminescence is traced in the background. Excitation at 280 nm. Slit widths: 13 nm (Ex/Em).

(Figure 6). As observed in other reported CPL-active terbium complexes, the ${}^{5}D_{4} \rightarrow {}^{4}F_{5}$, ${}^{5}D_{4} \rightarrow {}^{4}F_{4}$, and ${}^{5}D_{4} \rightarrow {}^{4}F_{3}$ transitions (545, 585, and 624 nm, respectively) exhibit trisignate patterns with strong dissymmetry factors ($g_{lum} = 10.161$, 10.071, and 10.101, respectively). Drastically lower g_{lum} values (~10.021) are observed for the ${}^{5}D_{4} \rightarrow {}^{4}F_{6}$ and ${}^{5}D_{4} \rightarrow {}^{4}F_{1}$ transitions at 491 and 670 nm, respectively. More surprisingly, the weakly emissive ${}^{5}D_{4} \rightarrow {}^{4}F_{2}$ transition at 653 nm exhibits a very strong CPL signal following a trisignate pattern with a g_{lum} of 10.221. The stronger CPL signal is not consistent with the transition rules described by Richardson,²² because the ${}^{5}D_{4} \rightarrow {}^{4}F_{2}$ transition should be of the same type as the weakly CPLactive ${}^{5}D_{4} \rightarrow {}^{4}F_{6}$ transition. Our observations imply that the crystal field is significantly perturbing the system into generating stronger dissymmetry factors.

Because of the unusually strong CPL signals observed in some transitions of both europium and terbium species, we also investigated the dysprosium complexes ((R,R)-tpdac)Dy- $(OTf)_3$ and ((S,S)-tpdac)Dy $(OTf)_3$. Both enantiomers displayed mirror image CPL spectra (Figure 7), and the most CPL-active transition was the ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition at 665 nm, with a strong g_{lum} of l0.16l. Only a few examples of dysprosium complexes exhibiting CPL have been reported, with dissymmetry factors ranging from 0.012 to 0.013²³ to 0.4.²⁴ Smaller dissymmetry factors for the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (479 nm) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) transitions were also observed ($g_{lum} = |0.05|$ and |0.03|, respectively). The CPL magnitudes observed are, this time, consistent with the expected rotatory strength of the transitions.²²

CONCLUSION

We have demonstrated that enantiopure N,N,N',N'-tetrakis(2pyridylmethyl)-*trans*-1,2-diaminocyclohexane (tpdac) is a competent ligands for lanthanide binding and sensitization, and that the corresponding complexes emit circularly polarized luminescence with strong dissymmetry factors. The combination of ¹H NMR, single-crystal X-ray diffraction, and luminescence studies provided evidence of the existence of a single C_2 -symmetrical species in solution. Unusually strong dissymmetry factors were also observed for some transitions typically associated with weaker g_{lum} values, notably for europium and terbium, and indicate that these transitions should not be overlooked in future studies. Derivatives of the tpdac ligand presented here are synthetically accessible and open the possibilities for fine-tuning the ligand toward obtaining higher quantum yields and dissymmetry factors.

EXPERIMENTAL SECTION

General Methods, Materials, and Instrumentation. All manipulations were carried out air free in a Vigor glovebox or using Schlenk techniques. The $Eu(OTf)_3$ and $Dy(OTf)_3$ were purchased from Alfa Aesar. The $Tb(OTf)_3$ was purchased from StremChemicals. The cetyltrimethylammonium chloride was purchased from Sigma-Aldrich. Sm(OTf)_3, (*R*,*R*)-(1,2)-diaminocyclohexane, (*S*,*S*)-(1,2)-diaminocyclohexane, and 2-chloromethylpyridine hydrochloride were purchased from Oakwood Chemicals.

All materials were used without further purification aside from the (1,2)-diaminocyclohexanes that were sublimed and then stored under an inert atmosphere to prevent absorption of water. All solvents used in syntheses were dried using a solvent purification system from Pure Process Technology or distilled under nitrogen after being stirred overnight with calcium hydride.

The chiral tetrakis(2-pyridylmethyl)diaminocyclohexane ligands (tpdac) were synthesized in a manner similar to that of the tpen ligand previously reported. 13

NMR Spectroscopy. All NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. Chemical shifts are reported in parts per million relative to the residual nondeuterated solvent peak for ¹H and relative to $BF_3(C_4H_{10}O)$ for ¹⁹F.

Optical Rotation. Specific rotations for compounds were measured using a JASCO P-2000 polarimeter with a tungstenhalogen source reading at 589 nm. For the respective concentrations of each solution, see this section.

Photophysical Studies. All photophysical studies are performed in sealed cuvettes under an atmosphere of dry dinitrogen using anhydrous acetonitrile.

Absorption, excitation, and emission spectra were recorded on a HORIBA Duetta Spectrophotometer using HORIBA EzSpec Software. This spectrophotometer is a dual fluorimeter/ultraviolet-visible instrument equipped with a CCD detector. The measurement of the absorbance is read 180° from the excitation, and the fluorescence is taken from a secondary detector 90° offset of the excitation. Fluorescence values with correction for absorbance were collected for all samples.

Circularly polarized luminescence was measured on an OLIS CPL Solo. For more information about the Solo, see page S26 of the Supporting Information.

Quantum yields were determined using two methods. Absolute quantum yields were determined using an Edinburgh FLS1000 spectrophotometer equipped with a PMT 980 detector and a barium sulfate-coated integrating sphere using the Fluoracle software. External quantum yields were obtained using 9,10-diphenylanthracene as a standard (see pages S26 and S27 of the Supporting Information). Lifetimes for each complex were determined using an excitation wavelength of 280 nm on an OLIS CPL Solo utilizing the Globalworks and Photon Counting Phosphorescence (PCPH) Lifetime Software. For individual sample conditions for each wavelength, see pages S12–S22 of the Supporting Information.

Mass Spectrometry. High-resolution mass spectrometry was conducted for each complex using an Applied Biosystems Sciex Qstar Elite LC mass spectrometer.

Single-Crystal X-ray Crystallography. Single-crystal X-ray diffraction studies were performed at Vanderbilt University. A suitable crystal of each sample was selected for analysis and mounted in a polyimide loop. All measurements were taken on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Mo K α radiation at a temperature of 100 K. Using Olex2,²⁵ the structure was determined with the ShelXL structure solution program using direct methods and refined with the ShelXL refinement package²⁶ using least-squares minimization.

CCDC 1970322 [((R,R)-tpdac)Eu(OTf)₃] and 1970321 [((S,S)-tpdac)Eu(OTf)₃] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center.

Synthetic Procedures and Characterizations. (R,R)-N,N,N',N'-Tetrakis(2-pyridylmethyl)-trans-1,2-diaminocyclohexane, (R,R)tpdac. The synthesis for the tpdac ligand was conducted in a manner similar to that of the tpen analogue previously reported.¹³ To a 100 mL flame-dried Schlenk flask fit with a stir bar was added 2chloromethylpyridine hydrochloride (6.91 g, 0.042 mol, 4.04 equiv), and the flask was evacuated and placed under nitrogen. The solid was then dissolved in 5 mL of degassed deionized water, and 10 mL of a 5 M NaOH solution was added until the color changed to dark redbrown. (*R*,*R*)-1,2-Diaminocyclohexane (1.19 g, 0.01 mol, 1 equiv) was dissolved in 8 mL of dry, degassed dichloromethane (DCM) and added to the reaction flask. A second 10 mL portion of NaOH solution was added (0.10 mol, 9.6 equiv total) followed by 0.5 mL of a 25% cetyltrimethylammonium chloride solution (121 mg, 0.378 mmol, 0.036 equiv). The flask was covered in foil and stirred for 72 h under nitrogen. The reaction mixture was then extracted three times with 20 mL of DCM, and the organic layer was washed three times with deionized water and then dried with sodium sulfate. The solvent was removed in vacuo, and the solid residue was extracted with hexanes and left to slowly evaporate. Colorless to slightly yellow crystals were obtained in two crops: yield 2.52 g, 50.5%; ¹H NMR (CD₃CN, 400 MHz) δ 1.13 (m, 4H, -CH_{2(CHx)}), 1.72 (m, 2H, $-CH_{2(CHx)})$, 2.16 (d, J = 11.6 Hz, 2H, $-CH_{2(CHx)})$, 2.78 (m, 2H, $-CH_{2(CHx)}$), 3.60 (d, J = 14.4 Hz, 4H, $-NCH_{2}Pyr$), 3.72 (d, J = 14.4, 4H, -NCH₂Pyr), 7.12 (t, J = 5.6, 6.4 Hz, 4H, CH_{pyr}), 7.49 (dt, J = 1.6, 7.6 Hz, 4H, CH_{pyr}), 7.62 (d, J = 8 Hz, 4H, CH_{pyr}), 8.41 (d, J = 4.4 Hz, 4H, CH_{pvr}); $[\alpha]_D$ (c = 0.48 in ACN) +5.48 first crop, (c = 0.63 in ACN) +6.18 second crop.

(*S*,*S*)-*N*,*N*,*N*',*N*'-*Tetrakis*(2-*pyridylmethyl*)-*trans*-1,2-*diaminocyclohexane*, (*S*,*S*)-*tpdac*. The synthesis of the enantiomer was the same as described above: yield 3.28 g, 65.8%; ¹H NMR (CD₃CN, 400 MHz) δ 1.13 (m, 4H, -CH_{2(CHx})), 1.72 (m, 2H, -CH_{2(CHx})), 2.16 (d, *J* = 11.6 Hz, 2H, -CH_{2(CHx})), 2.78 (m, 2H, -CH_{2(CHx})), 3.60 (d, *J* = 14.4 Hz, 4H, -NCH₂Pyr), 3.72 (d, *J* = 14.4, 4H, -NCH₂Pyr), 7.12 (t, *J* = 5.6, 6.4 Hz, 4H, CH_{pyr}), 7.49 (dt, *J* = 1.6, 7.6 Hz, 4H, CH_{pyr}), 7.62 (d, *J* = 8 Hz, 4H, CH_{pyr}), 8.41 (d, *J* = 4.4 Hz, 4H, CH_{pyr}); $[\alpha]_D$ (*c* = 0.52 in ACN) – 5.12.

((R,R)-tpdac)Sm(OTf)₃. The synthesis of the samarium (R,R)-tpdac salt was conducted in the same manner as its tpen analogue previously reported.¹³ To a 20 mL scintillation vial in the glovebox were added (R,R)-tpdac (184 mg, 0.38 mmol, 1 equiv) with a stir bar and 3 mL of dry ACN. Next, samarium(III) trifluoromethanesulfonate was weighed into a 4 mL vial (230 mg, 0.38 mmol, 1.0 equiv) and added as a solid to the stirring reaction mixture. The solid dissolved quickly reacting with the ligand, and the reaction mixture was used to rinse the 4 mL vial to ensure full transfer of the samarium salt and stirred overnight. The solution was then filtered and pumped in vacuo to remove solvent to give a white crystalline solid (380 mg, 92%). Crystals for photophysical studies were obtained by slow diffusion of

ether into a dilute solution in dimethoxyethane: ¹H NMR (CD₃CN, 400 MHz) δ 11.3 (s [br], CH_{pyr}, 2H), 8.35 (t, *J* = 7.6 Hz, CH_{pyr}, 2H), 8.04 (dd, *J* = 5.2, 6.8 Hz, CH_{pyr}, 2H), 7.92 (d, *J* = 8.0 Hz, CH_{pyr}, 2H), 7.48 (s [br], -NCH₂Ar, 2H), 7.39 (t, *J* = 7.6 Hz, CH_{pyr}, 2H), 6.90 (dd, *J* = 6.0, 6.4 Hz, CH_{pyr}, 4H), 6.45 (d, *J* = 7.6 Hz, CH_{pyr}, 2H), 5.43 (s [br], -CH₂(CH_x), 2H), 4.48 (d, *J* = 15.2 Hz, -NCH₂Ar, 2H), 3.27 (d, *J* = 16.8 Hz, -NCH₂Ar, 2H), 2.93 (d, *J* = 12.0 Hz, -CH₂(CH_x), 2H), 2.63 (s [br], -CH₂(CH_x), 2H), 2.17 (d, *J* = 8.4 Hz, -CH₂(CH_x), 2H), 1.77 (t, *J* = 8.4 Hz, -CH₂(CH_x), 2H), -0.24 (s [br], -NCH₂Ar, 2H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -79.2 (s, 9F, -OSO₂CF₃); [*α*]_D (*c* = 0.66 in ACN) +5.91; HRMS calcd for C₃₂H₃₄F₆N₆O₆S₂Sm⁺ ([M - (-OSO₂CF₃)]⁺) 928.1077, found 928.0810. Anal. Calcd for C₃₃H₃₄F₉N₆O₉S₃Sm: C, 36.83; H, 3.18; N, 7.81. Found: C, 36.22; H, 3.11; N, 7.77.

 $((S,S)-tpdac)Sm(OTf)_3$. The synthesis of the samarium complex with the (S,S)-tpdac ligand is identical to that of its (R,R)-tpdac analogue: yield 95%; ¹H NMR (CD₃CN, 400 MHz) δ 11.3 (s [br], CH_{pyr}, 2H), 8.35 (t, J = 7.6 Hz, CH_{pyr}, 2H), 8.04 (dd, J = 5.2, 6.8 Hz, CH_{pyr} , 2H), 7.92 (d, J = 8.0 Hz, CH_{pyr} , 2H), 7.48 (s [br], NCH₂Ar, 2H), 7.39 (t, J = 7.6 Hz, CH_{pyr}, 2H), 6.90 (dd, J = 6.0, 6.4 Hz, CH_{pyr}, 4H), 6.45 (d, J = 7.6 Hz, CH_{pyr} , 2H), 5.43 (s [br], $-CH_{2(CHx)}$, 2H), 4.48 (d, J = 15.2 Hz, -NCH₂Ar, 2H), 3.27 (d, J = 16.8 Hz, -NCH₂Ar, 2H), 2.93 (d, J = 12.0 Hz, -CH_{2(CHx)}, 2H), 2.63 (s [br], -CH_{2(CHx)}, 2H), 2.17 (d, J = 8.4 Hz, $-CH_{2(CHx)}$, 2H), 1.77 (t, J = 8.4 Hz, -CH_{2(CHx)}, 2H), -0.24 (s [br], -NCH₂Ar, 2H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -79.2 (s, 9F, -OSO₂CF₃); [α]_D (c = 0.60 in ACN) -7.46; HRMS calcd for $C_{32}H_{34}F_6N_6O_6S_2Sm^+$ ([M - (-OSO_2CF_3)]⁺) 928.1077, found 928.1048. Anal. Calcd for C33H34F9N6O9S3Sm: C, 36.83; H, 3.18; N, 7.81. Found: C, 36.99; H, 3.23; N, 7.91.

((*R*,*R*)-*tpdac*)*Eu*(*OTf*)₃. The synthesis of the europium complex with (*R*,*R*)-*tpdac* is identical to that of ((*R*,*R*)-*tpdac*)Sm(OTf)₃ above, substituting a europium triflate salt: yield 96%; ¹H NMR (CD₃CN, 400 MHz) δ 12.19 (s [br], 2H), 10.94 (s [br], 2H), 10.23 (s [br], 2H), 8.98 (s [br], 2H), 5.73 (t, *J* = 8.0 Hz, 2H), 3.48 (s [br], 2H), 2.4 (s [br], 2H), 2.20 (s [br], 2H), 0.00 (d, *J* = 8.0 Hz, 2H), -1.55 (s [br], 2H), -2.35 (s [br], 2H), -2.91 (s [br], 2H), -3.16 (d, *J* = 12.0 Hz, 2H), -4.98 (s [br], 4H), -7.23 (s [br], 2H), -11.01 (s [br], 2H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -79.3 (s, 9F, -OSO₂CF₃); [*α*]_D (*c* = 0.58 in ACN) +6.56; HRMS calcd for C₃₂H₃₄F₆N₆O₆S₂Eu⁺ ([M - (-OSO₂CF₃)]⁺) 929.111, found 929.0637. Anal. Calcd for C₃₃H₃₄F₉N₆O₆S₃Eu: C, 36.78; H, 3.18; N, 7.80. Found: C, 37.01; H, 3.27; N, 7.91.

((*S*,*S*)-*tpdac*)*Eu*(*OTf*)₃. The synthesis of the europium complex with the (*S*,*S*)-tpdac ligand is identical to that of its (*R*,*R*)-tpdac analogue: yield 93%; ¹H NMR (CD₃CN, 400 MHz) δ 12.19 (s [br], 2H), 10.94 (s [br], 2H), 10.23 (s [br], 2H), 8.98 (s [br], 2H), 5.73 (t, *J* = 8.0 Hz, 2H), 3.48 (s [br], 2H), 2.4 (s [br], 2H), 2.20 (s [br], 2H), 0.00 (d, *J* = 8.0 Hz, 2H), -1.55 (s [br], 2H), -2.35 (s [br], 2H), -2.91 (s [br], 2H), -3.16 (d, *J* = 12.0 Hz, 2H), -4.98 (s [br], 4H), -7.23 (s [br], 2H), -11.01 (s [br], 2H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -79.3 (s, 9F, -OSO₂CF₃); [*α*]_D (*c* = 0.60 in ACN) -8.37; HRMS calcd for C₃₂H₃₄F₆N₆O₆S₂Eu⁺ ([M - (-OSO₂CF₃)]⁺) 929.111, found 929.1107. Anal. Calcd for C₃₃H₃₄F₉N₆O₉S₃Eu: C, 36.78; H, 3.18; N, 7.80. Found: C, 36.82; H, 3.17; N, 7.88.

((S,S)-tpdac)Gd(OTf)₃. The synthesis of the gadolinium complex with (S,S)-tpdac is identical to that of ((S,S)-tpdac)Sm(OTf)₃ above, substituting a gadolinium triflate salt: yield 95%; ¹H NMR (CD₃CN, 400 MHz) δ 13.21 (s [br], 2H), 8.22 (s [br], 4H), 7.94 (s [br], 6H), 7.44 (s [br], 12H), 3.40 (s [br], 4H), 2.30 (s [br], 4H), 0.92 (s [br], 2H).

((*R*,*R*)-tpdac)Dy(OTf)₃. The synthesis of the dysprosium complex with (*R*,*R*)-tpdac is identical to that of ((*R*,*R*)-tpdac)Sm(OTf)₃ above, substituting a dysprosium triflate salt: yield 97%; ¹H NMR (CD₃CN, 400 MHz) δ 162.3 (s [br], 2H), 116.52 (s [br], 2H), 92.29 (s [br], 4H), 76.69 (s [br], 2H), 71.38 (s [br], 2H), 53.78 (s [br], 4H), 38.18 (s [br], 4H), 18.47 (s [br], 4H), -37.85 (s [br], 4H), -41.17 (s [br], 2H), -196.86 (s [br], 4H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ

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-74.0 (s, 9F, $-OSO_2CF_3$); [*α*]_D (*c* = 0.60 in ACN) +6.78; HRMS calcd for C₃₂H₃₄F₆N₆O₆S₂Dy⁺ ([M − ($-OSO_2CF_3$)]⁺) 940.117, found 640.1074. Anal. Calcd for C₃₃H₃₄F₉N₆O₉S₃Dy: C, 36.42; H, 3.15; N, 7.72. Found: C, 36.55; H, 3.25; N, 7.90.

((*S*,*S*)-*tpdac*)*Dy*(*OTf*)₃. The synthesis of the dysprosium complex with the (*S*,*S*)-tpdac ligand is identical to that of its (*R*,*R*)-tpdac analogue: yield 94%; ¹H NMR (CD₃CN, 400 MHz) δ 162.3 (s [br], 2H), 116.52 (s [br], 2H), 92.29 (s [br], 4H), 76.69 (s [br], 2H), 71.38 (s [br], 2H), 53.78 (s [br], 4H), 38.18 (s [br], 4H), 18.47 (s [br], 4H), -37.85 (s [br], 4H), -41.17 (s [br], 2H), -196.86 (s [br], 4H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -74.0 (s, 9F, -OSO₂CF₃); [*α*]_D (*c* = 0.62 in ACN) -7.71; HRMS calcd for C₃₂H₃₄F₆N₆O₆S₂Dy⁺ ([M - (-OSO₂CF₃)]⁺) 940.117, found 640.1074. Anal. Calcd for C₃₃H₃₄F₉N₆O₉S₃Dy: C, 36.42; H, 3.15; N, 7.72. Found: C, 36.58; H, 3.30; N, 7.88.

((*R*,*R*)-*tpdac*)*Tb*(*OTf*)₃. The synthesis of the terbium complex with (*R*,*R*)-*tpdac* is identical to that of ((*R*,*R*)-*tpdac*)Sm(OTf)₃ above, substituting a terbium triflate salt: yield 98%; ¹H NMR (CD₃CN, 400 MHz) δ 241.65 (s [br], 2H), 202.57 (s [br], 2H), 184.84 (s [br], 2H), 109.10 (s [br], 4H), 70.03 (s [br], 2H), 65.22 (s [br], 2H), 57.71 (s [br], 2H), 43.88 (s [br], 4H), 18.35 (s [br], 4H), 0.16 (s [br], 2H), -27.65 (s [br], 2H), -31.26 (s [br], 2H), -61.61 (s [br], 4H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -73.7 (s, 9F, -OSO₂CF₃); [*α*]_D (*c* = 0.52 in ACN) +7.23; HRMS calcd for C₃₂H₃₄F₆N₆O₆S₂Tb⁺ ([M - (-OSO₂CF₃)]⁺) 935.113, found 935.0882. Anal. Calcd for C₃₃H₃₄F₉N₆O₉S₃Tb: C, 36.54; H, 3.16; N, 7.75. Found: C, 37.46; H, 3.35; N, 8.65. Anal. Found is more consistent with calcd for C₃₅H₃₇F₉N₇O₉S₃Tb (M + ACN): C, 37.63; H, 3.34; N, 8.78.

((*S*,*S*)-*tpdac*)*Tb*(*OTf*)₃. The synthesis of the terbium complex with the (*S*,*S*)-tpdac ligand is identical to that of its (*R*,*R*)-tpdac analogue: yield 95%; ¹H NMR (CD₃CN, 400 MHz) δ 241.65 (s [br], 2H), 202.57 (s [br], 2H), 184.84 (s [br], 2H), 109.10 (s [br], 4H), 70.03 (s [br], 2H), 65.22 (s [br], 2H), 57.71 (s [br], 2H), 43.88 (s [br], 4H), 18.35 (s [br], 4H), 0.16 (s [br], 2H), -27.65 (s [br], 2H), -31.26 (s [br], 2H), -61.61 (s [br], 4H); all efforts to obtain ¹³C NMR data were unsuccessful; ¹⁹F NMR (CD₃CN, 376.512 MHz) δ -73.7 (s, 9F, -OSO₂CF₃); [*α*]_D (*c* = 0.60 in ACN) -6.93; HRMS calcd for $C_{32}H_{34}F_6N_6O_6S_2Tb^+$ ([M - (-OSO₂CF₃)]⁺) 935.113, found 935.0098. Anal. Calcd for $C_{33}H_{34}F_9N_6O_9S_3Tb: C, 36.54; H, 3.16; N, 7.75.$ Found: C, 37.01; H, 3.21; N, 7.91.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00628.

NMR spectra, crystallographic parameters and refinement data, and additional spectroscopic data (PDF)

Accession Codes

CCDC 1970321–1970322 and 1995232 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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